Specific Heat of defects in the Haldane System Y_2BaNiO_5

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(Received February 7, 2008)

Abstract

We calculate the specific heat of the antiferromagnetic spin-1 chain compound $Y_2BaNi_{1-x}Zn_xO_5$ in the presence of a magnetic field. The low-energy spectrum of a Heisenberg Hamiltonian, which includes realistic anisotropies, has been solved using the density matrix renormalization group. The observed Schottky anomaly is very well described by this theory. For large chains ($N > 50$), contrary to previous interpretations of the specific heat data, we find $S = 1/2$ states. These results are thus also consistent with electron-spin-resonance data for NENP.

PACS numbers: 75.40 Cx, 75.10Jm, 75.40 Mg.

A great deal of interest in one dimensional Heisenberg chains with nearest-neighbor antiferromagnetic (AF) exchange coupling, J, has been originated by Haldane's conjecture that integer-valued spin chains would exhibit a gap in the spin-wave excitation spectrum [1], in contrast to half-integer spin chains which would be gapless [2] with a linear dispersion relation above the ground state. This quantum many-body phenomena is different from the usual source of gaps in magnets, namely, single-ion anisotropy, which does not involve correlation effects. Subsequent observations of large gaps in spin-1 quasi-one-dimensional systems present in the structure of some compounds like $CsNiCl_3$ [3], $[Ni(C_2HgN_2)_2(NO_2)]ClO_4$ (NENP) [4,5], and Y_2BaNiO_5 [6,7], have confirmed Haldane's observation.

Affleck *et al.* [8] have shown that the exact ground state of the Hamiltonian $\sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1} + (\mathbf{S}_i \cdot \mathbf{S}_{i+1})^2/3$ is a valence-bond-solid (VBS) state. In this state, each S =1 spin is represented by symmetrization of two $S = 1/2$ entities. These $S = 1/2$ spins at each site are coupled with nearest-neighbor $S = 1/2$ spins, one to the left and the other to the right, to form singlets. Hence, an open chain has two unpaired $S = 1/2$ spins, one at each end. They [8] have also proposed that the VBS state describes qualitatively the physics of the Heisenberg model (without the biquadratic term). In agreement with this proposal, exact diagonalization [9] of finite open chains shows that the four lowest-lying states are a triplet and singlet whose energy separation approaches zero exponentially with increasing length. Monte Carlo [10] and density-matrix renormalization-group (DMRG) [11] studies clearly show the presence of $S = 1/2$ end states. This picture is also supported by electron paramagnetic resonance (EPR) measurements of NENP doped with non-magnetic ions [12], where resonances corresponding to the fractional spin $S = 1/2$ states at the "open" ends of the Ni chains were observed.

However, Ramirez *et al.* [13] also tested the presence of free $S = 1/2$ states by studying the specific heat of defects in NENP and Y_2BaNiO_5, with magnetic fields up to 9T and temperatures down to 0.2K. On the basis of a comparison between two very simplified pictures, they found that the shape and magnitude of the Schottky anomaly associated with the defects in $Y_2BaNi_{1-x}Zn_xO_5$ are well described by a simple model involving spin-1

excitations, instead of the $S = 1/2$ excitations of the VBS. These results are in contrast with the above mentioned EPR measurements of NENP [12] .

While previous theoretical studies of the spin-1 Heisenberg chain [9–11] confirm the existence of free $S = 1/2$ spins at the ends of sufficiently long chains in agreement with the EPR measurements, it seems difficult to reconcile these results with the specific heat measurements and no theoretical calculation of the latter exists so far.

In this Letter, we solve the low energy spectrum of the appropriate Hamiltonian which describes the Ni chains of Y_2BaNiO_5 using DMRG and finite size scaling. Assuming that defects are randomly distributed (which leads to a Poisson distribution for the length of the open chains), we can calculate the specific heat for any concentration of non-magnetic impurities. Our results show that there is no contradiction between EPR [12] and specific heat measurements in $Y_2BaNi_{1-x}Zn_xO_5$ [13]. They confirm the existence of spin-$\frac{1}{2}$ excitations for sufficiently long chains and are in excellent agreement with the curves measured by Ramirez *et al.* [13].

Y_2BaNiO_5 has an orthorhombic crystal structure with the Ni^{2+} (S =1) ions arranged in linear chains with a nearest-neighbor AF superexchange coupling. The interchain coupling is more than three orders of magnitude weaker, making this compound an ideal one-dimensional antiferromagnetic chain. While each Ni atom is surrounded by six O atoms in near octahedron coordination, the true site symmetry is D_{2h}, and the appropriate Hamiltonian reads [14–16]:

$$H = \sum_i \{J\mathbf{S}_i \cdot \mathbf{S}_{i+1} + D(S_i^z)^2 + E[(S_i^x)^2 - (S_i^y)^2]\} - g\mu_B \mathbf{B} \cdot \mathbf{S}_{tot}$$

where z is along the chain axis and $\mathbf{S}_{tot}$ is the total spin. Recent estimates based on fits of the Haldane gaps (in x, y, and z directions) measured by inelastic neutron scattering , indicate $J \sim 280K$, $D \sim -.038J$, and $E \sim -.013J$ [14,15].

As pure Y_2BaNiO_5 has a Haldane gap $\sim 100K$ [7,14,15], the spin wave contribution to the specific heat $C(T)$ is negligible below $7K$. In this temperature range, $C(T)$ is dominated by the effect of the defects, which is manifested as a $1/T^2$ rise in $C(T)$, and a Schottky anomaly

in the presence of an applied magnetic field. The height and width of the Schottky anomaly strongly depends on the spin value of the low energy excitations. For these reasons, it is necessary to solve the low energy spectra ($\omega \leq 10K$) of H for all values of N to have an accurate theoretical picture.

By means of the DMRG method, we have calculated the two lower eigenenergies in the $S^z_{tot} = 0$ subspace and the lower one with $S^z_{tot} = 1$ (this state is degenerated with the $S^z_{tot} = -1$ due to the time-reversal symmetry of H) for all $N \leq 40$ and $E = 0$. The energy difference between the excited states and the ground state decays exponentially to zero with increasing N. This behavior, shown in Fig. 1 for an arbitrary value of anisotropy $D = -0.1$, allows us to extrapolate the energies to all values of $N > 40$, and demonstrate that the free S =1/2 spins at the end of the chain persist in presence of anisotropy. This issue is easy to understand considering that S =1/2 spins cannot be affected by anisotropy due to time-reversal symmetry. At this level, it is important to remark that the two S =1/2 spin excitations, predicted by VBS, have a finite localization length $l \sim 6$ sites [9–11]. Therefore, while they are nearly free for large ($N >> l$) open chains, the interaction between them is considerable when the length of the chain N is comparable to $2l$. This interaction splits the two S =1/2 states into a singlet (ground state for even N) and a triplet (ground state for odd N) one [17].

The difference between any two energies of the above mentioned low-energy states is linear in D, and the quadratic corrections are negligible [16]. This widely justifies the validity of perturbation theory to first order in D. By symmetry then we can include the term $\sum_i E[(S^x_i)^2 - (S^y_i)^2]$ to first order. Thus we find the following low-energy effective Hamiltonian including a spin $S = 1$ and a singlet state $|0\rangle$:

$$H_{eff} = (E_0(N) + \alpha(N)D)\,|0\rangle\,\langle 0| + D\beta(N)S^2_z$$
$$+E\beta(N)(S^2_x - S^2_y) - g\mu_B \mathbf{B}\cdot\mathbf{S}$$

where $E_0(N)$, $\alpha(N)$, and $\beta(N)$ are functions of the chain length N (determined from the DMRG data). The validity of the last term has been verified explicity by calculating the

matrix elements of S^+_{tot}, and S^-_{tot} for all chains. H_{eff} determines the thermodynamics of the system at temperatures well below the Haldane gap.

For a random distribution of defects, the specific heat per elementary cell of Zn-doped Y_2BaNiO_5 is:

$$C(B,T) = \sum_{N=1}^{\infty} x^2(1-x)^N \; C_N(B,T)$$

where $C_N(B,T)$ is the specific heat of a segment of length N described by H_{eff}, and x is the concentration of missing Ni atoms.

In order to minimize the effect of the lattice on $C(T)$, Ramirez *et al.* [13] plot the data, measured in $Y_2BaNi_{0.96}Zn_{0.04}O_5$, as the difference $[C(3\mathrm{T}) - C(6\mathrm{T})]/T$. In Fig. 2, we compare this difference calculated with H_{eff}, with the data taken from Ref. [13]. As the samples were powdered in order to ensure good thermal equilibration [13], the theoretical curve was obtained by averaging over all magnetic field directions. We have taken $J = 280K$, $D = -0.038J$ consistent with neutron scattering experiments [14,15] and $E = -0.032J$, somewhat larger than the experimental value. We have also considered $g = 2.35$ which is a reasonable value for the g factor [12,18]. The agreement between experiment and theory is excellent. Note that although the fit with the singlet-triplet model is good, the result we obtain here is better, particulary for temperatures around $0.5K$, and between 3 and $6K$. We also used a doping concentration of $x = 0.0428$ higher than the nominal value $x = 0.04$. This is due to the existence of native defects, also present in the pure compound. By fitting the data corresponding to pure Y_2BaNiO_5 we obtain $x = 0.0028$ instead of the value $x = 0.008$ obtained with the singlet-triplet model in Ref. [13] (see Fig. 3). Note that for small values of x, the height of the peak is proportional to x.

From Figs. 2 and 3 it is clear that the inclusion of interactions between end S =1/2 spins through the chain via the full Hamiltonian H, together with anisotropy, eliminates the apparent discrepancy between VBS theory predictions and measured specific heat [13]. In Fig. 4 we have separated the contributions of different chain lengths to $[C(3\mathrm{T}) - C(6\mathrm{T})]/T$. The full line corresponds to the result for non-interacting S =1/2 end spins. This behavior

is obtained for $N \gtrsim 50$ where the singlet-triplet gap is much smaller than $g\mu_B B$. The effect of anisotropy is stronger for shorter chains, changing the position and height of the Schottky peak. This behavior is mainly due to odd chains because they have an S =1 ground state. The anisotropy splits the $S_z = 0$ and $S_z = \pm 1$ (ground state for $D < 0$) triplet states, and the energy separation $\Delta(N)$ decreases with N (as can be inferred from Fig. 1). As one can see from Fig. 4, for large chains ($N > 30$), the result approaches asymptotically the VBS prediction, *i.e.* the peak is higher and shifted to slightly smaller temperatures as compared to the experimental result. However, the curves for shorter chains ($\Delta(N) \gtrsim g\mu_B B$) show the opposite behavior, and both tendencies are compensated in the final result. To understand this effect let's consider the simplest case of $E = B_x = B_y = 0$ and odd N . The energy difference corresponding to the Schottky anomaly, $E(S_z = 0) - E(S_z = -1)$, becomes $g\mu_B B_z + \Delta(N)$ when a magnetic field is applied. This explains the shift to the right registered for the shorter chains. As a consequence, the sum over small ($N \lesssim 20$) values of N, weighted with the Poisson distribution, yields a Schottky peak of larger width and lower height . The anomalous features at low temperature in Figs. 2 and 4 are due to the contributions of chains with even N for which the difference between the energy of the triplets with $S_z = \pm 1$ and the singlet ground state becomes of the order of the Zeeman energy $g\mu_B B$. For $6T$ this crossing occurs for N between 18 and 20 giving rise to the large negative contribution for the corresponding curve in Fig. 4. For $B = 3T$ the crossing occurs for N between 22 and 24 (see the $21 \leq N \leq 30$ curve in the same figure).

Our results allow us to understand why the $S = 1$ states of short chains were not seen [19] in the EPR experiments in NENP [12]. For $D/J \sim 0.2$ the splitting $\Delta(N)$ is greater or of the order of the applied magnetic field $g\mu_B B_a$ ($B_a \sim 0.35$T) when $N < 38$, while for $N > 54$, $\Delta(N) < 0.1 g\mu_B B_a$. These larger chains (76% of the total number of chains for $x = 0.005$) contribute to the same EPR signal with total weight 0.0038 per transition metal atom. On the other hand, each of the chains with $N < 38$ (weight $\lesssim .0002$), give place to a different gyromagnetic frequency larger than the one they considered [12].

In conclusion, by solving the low-energy spectrum of a Heisenberg Hamiltonian H which

includes axial and planar anisotropy we have reproduced the low-temperature and high-field specific-heat data measured in $Y_2BaNi_{1-x}Zn_xO_5$ [13]. Our results are consistent with valence-bond-solid predictions of S =1/2 end chain excitations, which are asymptotically free for large chain segments. However, their interaction for short segments are critical for the understanding of the specific heat behavior. These results remove the apparent discrepancy between the specific heat data for Y_2BaNiO_5, interpreted in Ref. [13] with a singlet-triplet model, and electron paramagnetic resonance data for NENP.

We would like to thank E. R. Gagliano for useful discussions. K.H. and C.D.B. are supported by Consejo Nacional de Investigaciones Cientifícas y Técnicas (CONICET), Argentina. A.A.A. is partially supported by CONICET.

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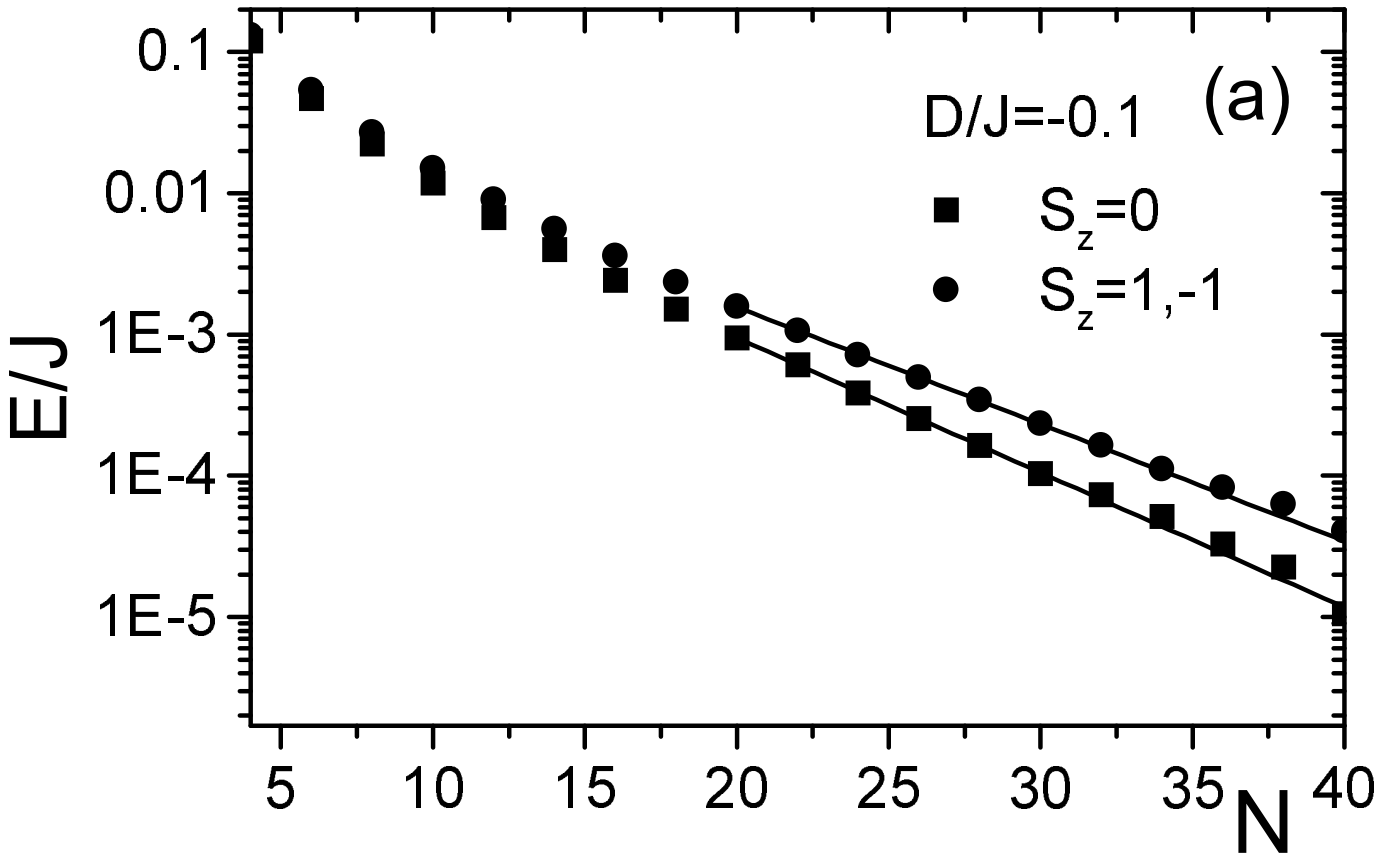
[19] The $S = 1$ spins (as opposed to $S = 1/2$) are affected by anisotropy and to first order the splittings generated by an applied magnetic field are independent of microwave frecuency contrary to what is observed [12].

Figure 1: Difference between the energy of the triplet $S_z = \pm 1$ ($S_z = 0$) and the singlet states in the presence of anisotropy D are denoted with circles (squares) . a) N even, b) N odd. The full line is an exponential fit of these differences for $N \geq 19$.

Figure 2: Specific heat difference between 3 and $6T$ for $Y_2BaNi_{0.96}Zn_{0.04}O_5$ [13]. The dashed and solid lines correspond to fits with the prediction of H ($J = 280K,\ D = -0.038J,\ E = -.032J,\ x = 0.0428,\ g = 2.35$) and the singlet-triplet model ($x = 0.048$).

Figure 3: Specific heat difference between 3 and $6T$ for undoped Y_2BaNiO_5. Solid circles are experimental data [13]. The solid line corresponds to a fit with the prediction of H for the same parameters as in Fig. 2 except for $x = 0.0028$, and the dashed line to the singlet-triplet model with $x = 0.008$.

Figure 4: Contributions of chains in different length intervals to the specific heat difference between 3 and 6T calculated with H for the same parameters as Fig. 2. The full line corresponds to the prediction of VBS theory for non-interacting $S = 1/2$ moments. The final result is obtained adding each curve with the weight denoted inside the figure.



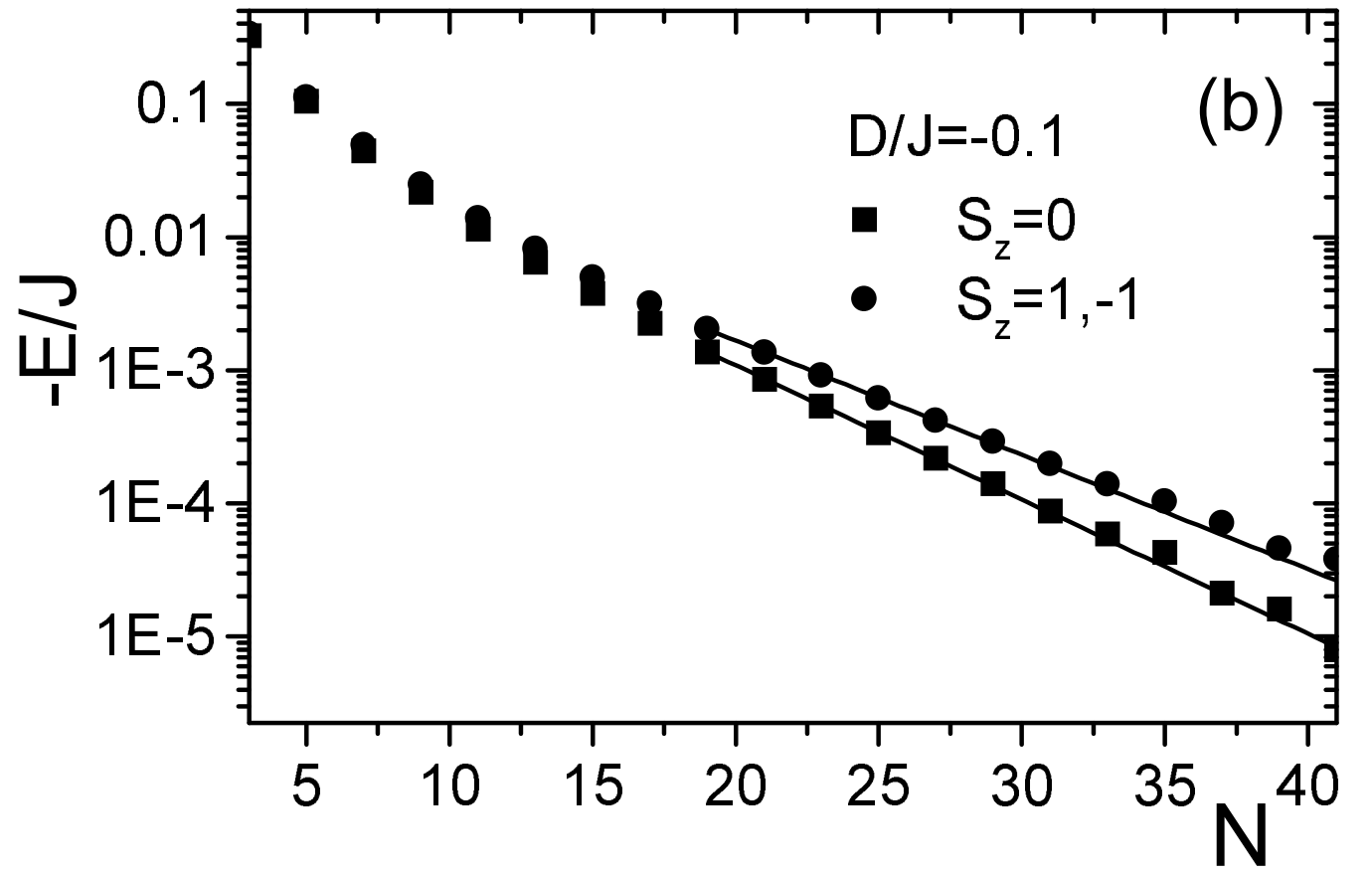


Fig. 1 Hallberg et. al.

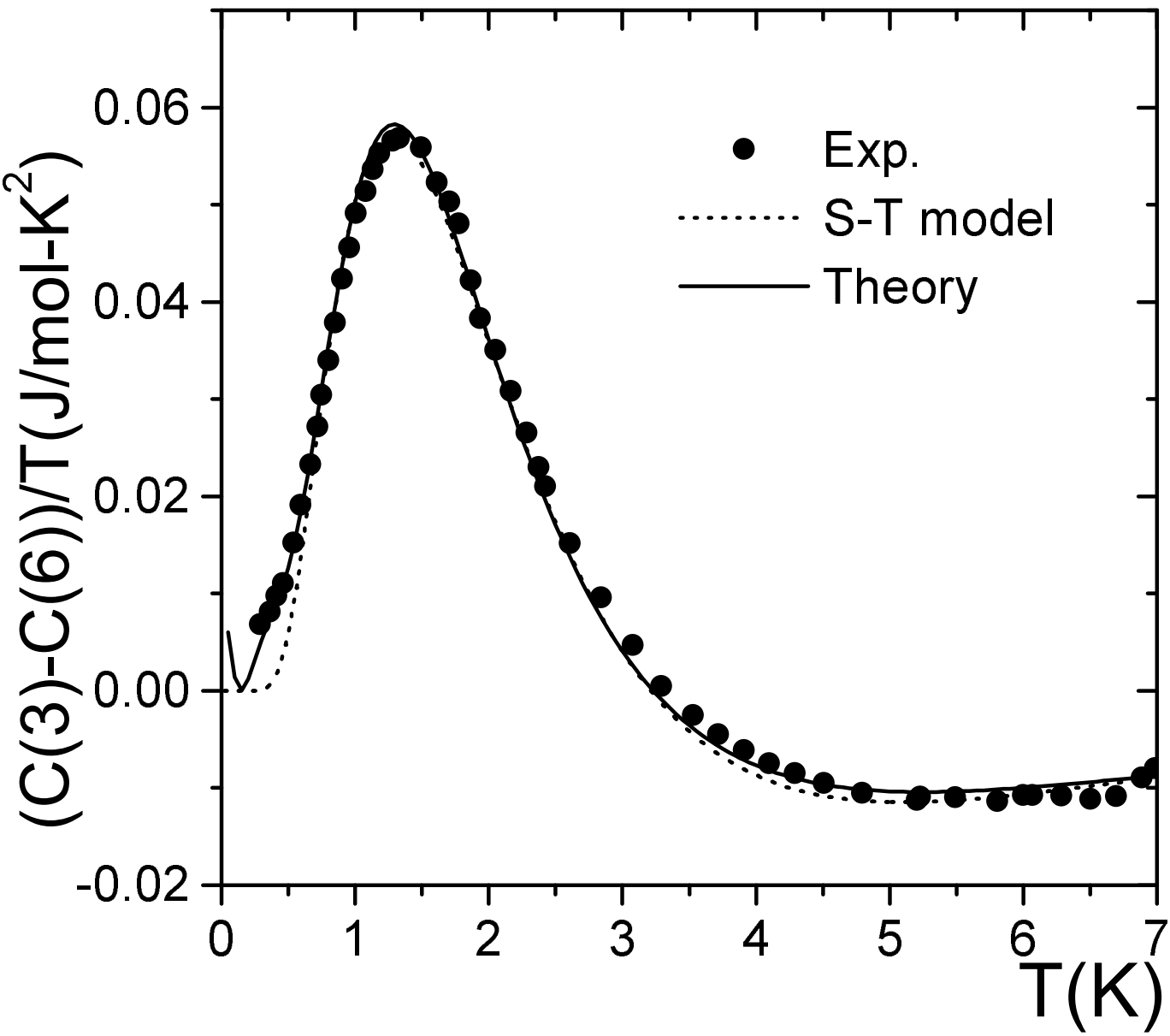
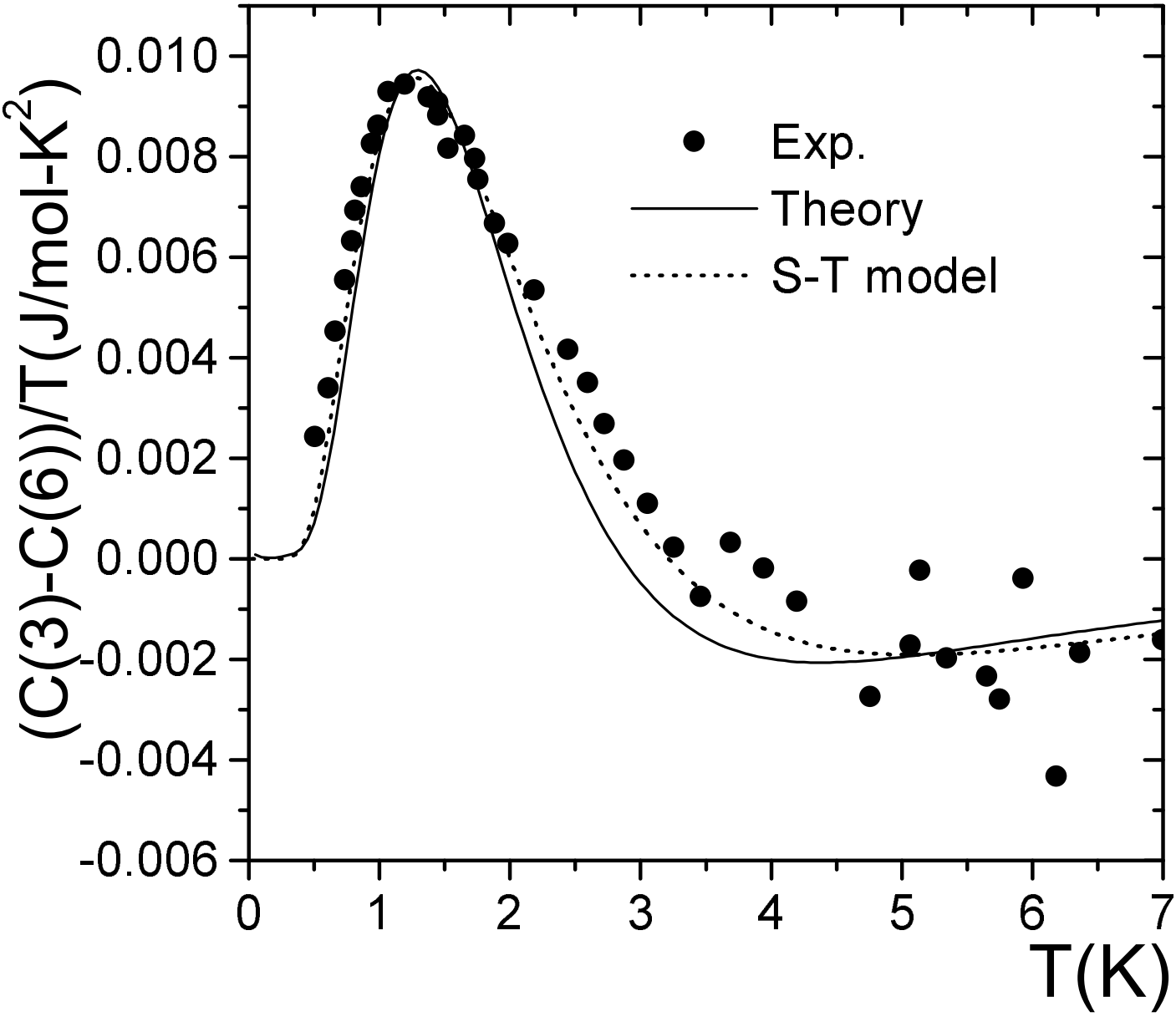


Fig. 2 Hallberg et. al.



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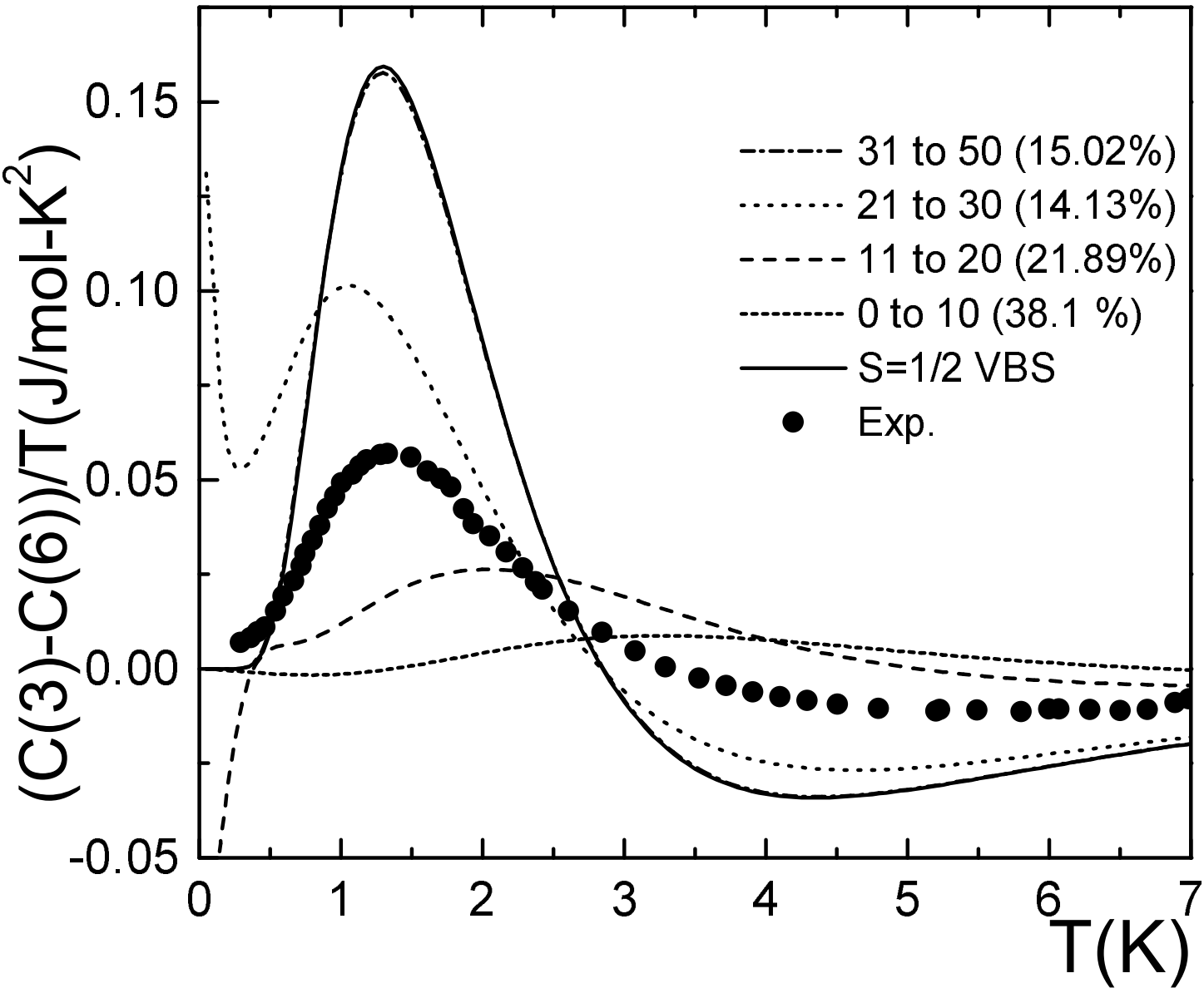

Fig. 4 Hallberg et. al.